

**FINAL REPORT
PHASE IV**

JULY 1982 - APRIL 1986

DOE/JPL CONTRACT 954334

62

+ Foreign

FLUID BED SILANE DECOMPOSITION R&D

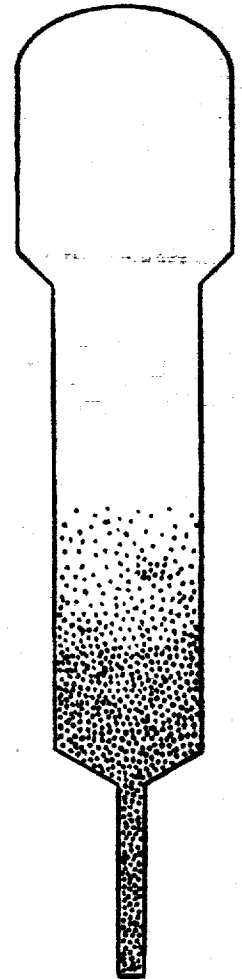
SOLAR ARRAY PROJECT

(NASA-CR-199905) FLUID BED SILANE
DECOMPOSITION R AND D: FLAT PLATE
SOLAR ARRAY PROJECT Final Report,
Jul. 1982 - Apr. 1986 (Union
Carbide Corp.) 77 p

N75-70373

Unclass

29/44 0101117



FLUID BED SILANE DECOMPOSITION R&D

FINAL REPORT FOR PHASE IV

JULY 1982 - APRIL 1986

DOE/JPL CONTRACT 954334

FLAT PLATE SOLAR ARRAY PROJECT

PREPARED BY

UNION CARBIDE CORPORATION

ELECTRONIC MATERIALS TECHNICAL CENTER

WASHOUGAL, WASHINGTON

AUGUST 1986

<u>SECTION</u>	<u>PAGE</u>
Abstract	i
1.0 Introduction	1
1.1 Background	1
1.2 Summary of Fluid Bed R&D	4
2.0 Description of Fluid Bed PDU	7
2.1 Process Description	7
2.2 Fluid Bed Reactor Components	10
2.2.1. Reactor Shell and Heaters	10
2.2.2 Liner and Seals	13
2.2.3 Feed Gas Plenum and Distributor	13
2.2.4. Deentrainment Section	14
2.2.5. Product Particle Segregation Section (Boot Section)	14
2.2.6. Produce Particle Cooling Chamber	14
2.2.7. Product Withdrawal Valve Train	15
2.2.8. Downstream Cooler and Filters	15
2.2.9. Analytical Instrumentation	15
2.2.10. Data Acquisition Equipment	17
2.3 Operating Parameters	17
2.3.1 Pressure and Temperature	17
2.3.2 Gas Velocities	18
2.3.3 Distributor Plate Temperature	20
2.3.4 Particle Segregation Section	20

CONTENTS

<u>SECTION</u>	<u>PAGE</u>
2.4 Outline of Operating Procedures	21
2.4.1 Introduction	21
2.4.2 Operation	21
2.4.2.1 Liner Loading	21
2.4.2.2 Evacuation	21
2.4.2.3 Purge Flows	22
2.4.2.4 Initial Heat Up	22
2.4.2.5 Analytical Instrument Calibration	23
2.4.2.6 Final Heatup and Hydrogen Fluidization	23
2.4.2.7 Software Startup	23
2.4.2.8 Distributor Cooling	23
2.4.2.9 Silane Addition	24
2.5 Operation	24
2.5.1 Maintaining Operating Parameters, Areas Requiring Frequent Checks	24
2.5.2 Product Withdrawal	26
2.5.3 Filter Backblowing	26
2.6 Controlled Shutdown	27
3.0 Experimental Studies	28
3.1 Seed Preparation System	28

CONTENTS

<u>SECTION</u>	<u>PAGE</u>
3.2 Summary of Experimental Runs	30
3.2.1 Experimental Run Summary H-05	31
3.2.2 Experimental Run Summary H-08	34
3.2.3 Experimental Run Summary J-02	36
3.2.4 Experimental Run Summary J-03	39
3.2.5 Experimental Run Summary K-01	40
4.0 Discussion of Results	43
4.1 Particle Growth and Powder Formation	43
4.2 Powder Formation	43
4.3 Silane Feed Concentration	45
4.4 Product Morphology	49
4.5 Chemical Analysis of Samples	54
4.5.1 Seed Purity Results	54
4.5.2 Analysis of Early Seed Material	54
4.5.3 Analyses of Recent Seed Material and Product	55
4.6 Single Crystal Growth	60
5.0 Technical Assessment	61
5.1 Process	61
5.2 Economics	62
6.0 Conclusions and Recommendations	64
7.0 References	66

LIST OF FIGURES

<u>FIGURE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
Figure 1	P&I Diagram for Fluid Bed PDU	8
Figure 2	Fluid Bed PDU Reactor with Liner	11
Figure 3	Gas Distributor	12
Figure 4	Product Withdrawal System	16
Figure 5	Particle Growth Rate for Run J-02	48

LIST OF TABLES

<u>TABLE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
Table 1	Product, Run H-05	33
Table 2	Product Weight Fractions, Run H-08	35
Table 3	Bed Material for Run J-02	38
Table 4	Run J-02, Product Sizes	38
Table 5	Summary of Recent Runs with Average Silane Feed Concentrations	47
Table 6	Seed Material Analytical Results	56
Table 7	Purity Analysis for Seed and Product Samples for Run H-04 by SSMS	57
Table 8	Purity Analysis for Seed and Product Samples for Runs J-02, J-03, K-01 by SSMS	58
Table 9	Purity Analysis for Product Samples from Runs J-03 and K-01 by NAA	59

LIST OF PHOTOS

<u>PHOTO NO.</u>	<u>TITLE</u>	<u>PAGE</u>
Photo 1	Product	51
Photo 2	Product Surface	51
Photo 3	Shattered Product Particle	52
Photo 4	Particle Cross Section	52
Photo 5/6	SEM Pictures of Product from Run J-02	53

FLUID BED SILANE DECOMPOSITION R&D

FLAT PLATE SOLAR ARRAY PROJECT

FINAL REPORT (PHASE IV)

PERIOD COVERED: JULY 1982 - APRIL 1986

JET PROPULSION LABORATORY (JPL) CONTRACT 954334

ABSTRACT

The commercial production of low-cost semiconductor-grade silicon is an essential requirement of the JPL/DOE (Department of Energy) Flat-Plate* Solar Array (FSA) project. A 1000 metric ton per year commercial facility using the Union Carbide Silane Process was estimated to produce molten silicon for a price of \$7.56/Kg (1975 dollars, private financing), meeting the DOE goal of less than \$10/Kg.

During Phases I and II (refer to June 1979 Final Report), the basic technology was demonstrated by laboratory experiments that silane can be produced via a closed-loop chemical process. The objective of Phase III (refer to April 1979-December 1981 Final Report) was the establishment of the practicality of a process producing semiconductor-grade silicon by a two-step process, the preparation of silane and the subsequent pyrolysis of silane to yield high-purity silicon.

* Formerly called "Low Cost Solar Array Project"

Under Phase IV, a continuation of contract 954334 for the period July 1982 through April 1986, work was performed on Fluid Bed Silane Decomposition by Union Carbide Corporation for the Jet Propulsion Laboratory. This contract had the overall objective of developing the process technology for the production of semiconductor grade polycrystalline silicon in a large commercial plant by 1986, at a price of not more than \$14/Kg of silicon based on 1975 dollars. The fluid bed reactor R&D program had the objective of demonstrating process feasibility by conducting long duration test runs and evaluating product samples. The results from the work demonstrated that a unit could be operated under steady-state conditions while achieving virtually complete silane conversion in the bed. The feasibility of growing a dislocation-free, high-resistivity, single crystal from the fluid bed product was shown.

1.0 INTRODUCTION

This report presents the summary of R&D work performed on Fluid Bed Silane Decomposition by Union Carbide Corporation for the Jet Propulsion Laboratory (JPL) under Phase IV continuation of contract 954334 during the period July 1982 through April 1986. This contract, a part of the JPL/Department of Energy (DOE) Flat Plate Solar Array (FSA) Project, had the overall objective of developing the process technology for the production of semiconductor grade polycrystalline silicon in a large commercial plant by 1986, at a price of not more than \$14 per kilogram of silicon based on 1975 dollars. The fluid bed reactor R&D program had the objective of demonstrating process feasibility by conducting long duration test runs and evaluating product samples.

1.1 BACKGROUND

Union Carbide Corporation was actively engaged in the development of the silane process under JPL/DOE FSA Project during the years 1975-1986. Contract 954334 covered work directed towards the specific needs of the FSA Project for meeting the goal of large volume, low cost production of semiconductor grade polycrystalline silicon for photovoltaic application.

The Phase I Program, started in 1975, established the feasibility of:

- The high-volume, low-cost production of silane, as an intermediate for obtaining semiconductor-grade silicon,

by the catalytic redistribution of chlorosilanes resulting from the reaction of hydrogen, m.g. silicon, and silicon tetrachloride.

- The subsequent pyrolysis of silane to semiconductor-grade silicon in free-space and fluidized-bed reactors.
- The high-frequency, capacitive heating of silicon seed particles suitable for silane pyrolysis in a fluidized bed.

The Phase II Program, building upon the promising technology base being developed under Phase I, was initiated in October 1977 and was conducted in parallel with the remaining Phase I effort. Phase II established:

- An information base for experimental silane and silicon facilities resulting from technical and experimental studies and engineering optimization.
- A preliminary design for an Experimental Process System Development Unit (EPSDU) capable of producing 100 metric tons of silane per year.
- An economic analysis to project product costs from commercial facilities.

The highly successful completion of the individual technical tasks that comprised Phase I and Phase II provided a firm technological and economic data base for Phase III. This phase, started in 1980, covered final design, construction, and test operation of a 100-ton EPSDU based on the silane-to-silicon process. The pilot plant was to be installed on the site of a Union Carbide facility in East Chicago, Indiana, and would have shared services with the existing facility. Shortly after

construction started, it was stopped because of reductions in contract funding.

The original intent of the DOE/JPL contract was to accelerate commercialization of the technology so that supplies of high-purity silicon could be made available for solar energy programs. Based on the work that had already been completed, Union Carbide elected to continue the pilot plant program using its own funds as the first step in commercialization. A licensing agreement was arranged with Komatsu Electronic Metals Company of Japan to obtain commercially proven technology and equipment for producing semiconductor-grade polysilicon from silane. Union Carbide's Electronic Division assumed responsibility for the program and proceeded with construction of the stand-alone EPSDU pilot plant in Washougal, Washington. Union Carbide's silane process, coupled with Komatsu's decomposition process, have been demonstrated to produce silane and silicon of very high purity.

Union Carbide's confidence that the integration of these two processes would be technically and economically viable resulted in accelerated planning for a large commercial plant. Design and construction of the 1200 metric ton facility at Moses Lake, Washington, were well underway before the pilot plant was operational. The Moses Lake facility was brought on-stream in early 1985.

Development of the fluid bed process for silane decomposition was pursued primarily under Phases III and IV of the JPL/DOE contract, and was initiated to provide a low cost method to produce polysilicon. The primary objectives of this R&D program were to

demonstrate process feasibility, determine a suitable operating window for the fluid bed reactor (FBR), conduct long-duration test runs, and demonstrate silicon purity. Details of this R&D work are outlined in this report.

Detailed discussion of the silane process development and EPSDU design are presented in References 1 and 2.

1.2 SUMMARY OF FLUID BED R&D

Under Phase III of the JPL/DOE contract, the fluid bed R&D effort consisted of the following:

- A bench-scale fixed bed deposition study to obtain silane reaction rate data, critical silane concentrations for heterogeneous decomposition, and silicon plating morphology data. This work, described in detail in Reference 3, showed the heterogeneous decomposition of silane to be first order with an activation energy of 38.8 K cal/mole. The data on critical silane concentrations were useful in projecting suitable operating conditions for a fluidized bed reactor to achieve complete silane conversion and good deposition morphology.
- Inert gas fluidization studies to test capacitive electrical heating techniques, and also to define fluidization parameters and conditions for preferential withdrawal of suitably large particles.
- Design, construction, and startup of a 6-inch diameter fluid bed process development unit (PDU) to decompose

silane and grow silicon particles. After the unit was started up and two shakedown runs were conducted, the PDU was shut down in May 1981 due to budgetary constraints.

Phase IV of the R&D program was carried out during the period July 1982 through April 1986, and consisted of the following activities:

- Transferring the fluid bed PDU from Union Carbide Corporation Tonawanda, New York, to Union Carbide's Electronic Materials Technical Center at Washougal, Washington, and reinstalling the PDU at the new facility.
- Operating the PDU with high purity silane, and identifying a suitable operating window in terms of bed temperature, feed silane concentration and fluidization velocity.
- Evaluating the purity of FBR product samples from the above runs.
- Designing and implementing a high-purity liner system to serve as an impurity barrier from the metal walls of the reactor.
- Conducting a series of long-duration experimental runs.
- Evaluating the purity of FBR product samples from the long-duration tests using quartz and polysilicon liners.

The results from the above work demonstrated that the PDU could be operated continuously for over 72 hours under steady conditions while achieving virtually complete silane conversion in the bed. The growth of particles up to 1000 microns from a

starting seed bed of mean size 300 microns was also demonstrated. Several kilograms of product generated were analyzed and also provided to JPL for it's evaluation. The feasibility of growing a dislocation-free, high-resistivity, single crystal from the fluid bed product was shown. The results have clearly demonstrated that the fluid bed process is well suited for producing high purity silicon material consistent with the FSA cost goals.

2.0 DESCRIPTION OF FLUID BED PDU

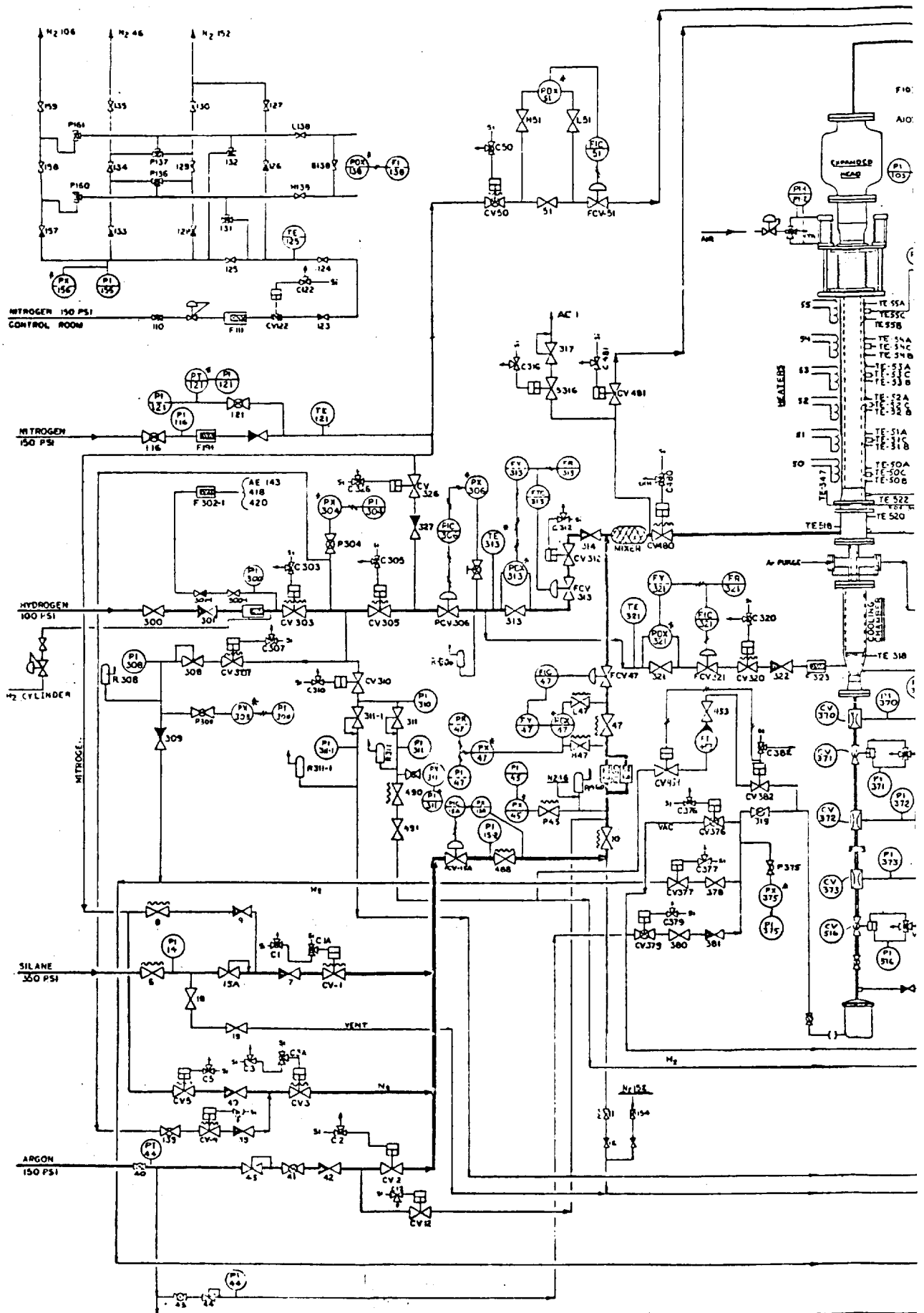
2.1 PROCESS DESCRIPTION

Fluid bed pyrolysis of silane involves the heterogeneous decomposition of silane gas on hot silicon seeds to produce free-flowing particles of silicon. The method offers the potential of converting high purity silane into semiconductor grade polycrystalline silicon material which can be directly processed by the Czochralski or ribbon growth technologies for single crystallization. This process also has the advantages of low capital and operating costs, making it attractive for meeting the low cost goals of the FSA program.

The fluid bed process utilizes thermal decomposition of the silane into solid silicon and hydrogen, i.e. $\text{SiH}_4(\text{g}) \rightarrow \text{Si}(\text{s}) + 2\text{H}_2(\text{g})$. This reaction occurs in two modes: heterogeneous and homogeneous decomposition. In the former, bed particle surfaces results in particle growth and useful product, while homogeneous decomposition occurring away from the particle surface in the gas phase results in the formation of fine powder. This powder is not useful product material, but proper reactor design and operation should minimize its formation. The decomposition reaction is irreversible and goes to completion at reactor temperature in the 600° to 750°C range.

A process flow diagram of the fluid bed PDU is shown in Figure 1.

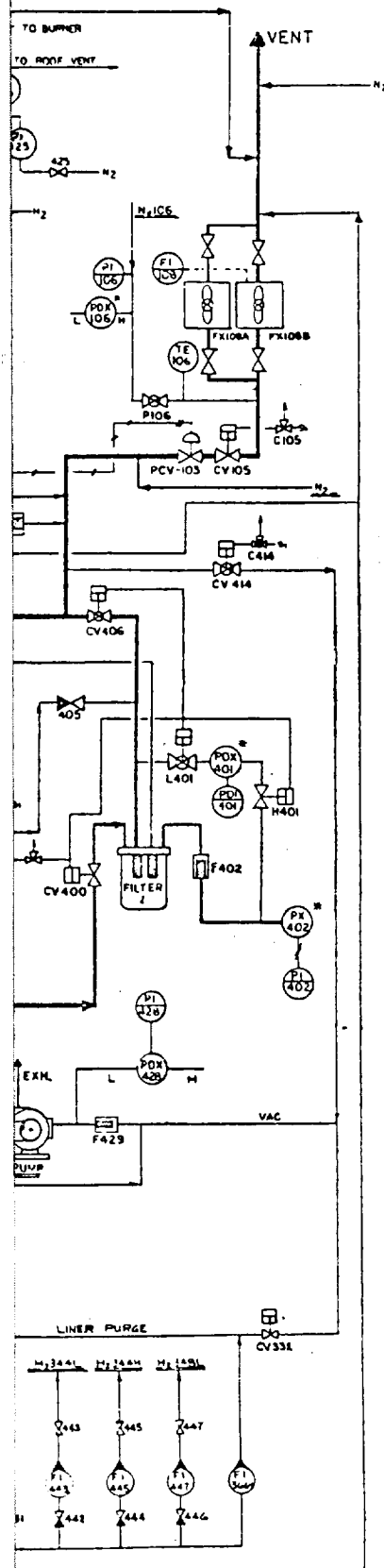
Silane from the building header is stepped down through valve 6 and pressure regulator 15A. Silane control pressure is held at 35



FOLDOUT FRAME

Figure 1

P&I DIAGRAM FOR FLI



FOLDOUT FRAME 2

psig using pressure control valve PCV-15A. Silane flow is monitored using the pressure drop across valve 47. Hydrogen is brought into the system in a similar manner. Hydrogen control pressure is held by PCV-306, and the pressure drop across valve 313 translates to hydrogen flow rate. The two gases are allowed to mix and are fed to this reactor through CV-480. Process hydrogen is also continuously fed through CV-320 to the bottom of the cooling chamber. This flow is used to fluidize bed material in the boot segregator section. Boot hydrogen flow rate is read as pressure drop across valve 321. Hydrogen is used as a purge gas through CV-310 and CV-440 for pressure sensing lines and the space between the reactor liner and shell. Filter backblowing is accomplished using hydrogen fed through CV-307 and CV-415. Reactor effluent is cooled, filtered and sent through a flowmeter to vent. Nitrogen is fed from CV-50 to dilute the exhaust gas and sweep out the vent stack.

The fluid bed PDU reactor consists of a vertical 6-inch diameter, electrically heated pipe which contains an internal high purity liner. It is partially filled with a bed of silicon seed particles. The bed sits on a feed gas distributor plate attached to the reactor bottom. A mixture of silane and hydrogen is fed through the distributor at sufficient rate to fluidize the bed of particles. The bed particles are heated by contact with the liner walls. The silane decomposes and deposits polysilicon on the bed particles. Bed material is periodically withdrawn as product out the reactor bottom. In the batchwise mode of reactor operation, the bed of seed material is grown to product size and then removed. However, in the continuous operation mode, seed particles are either internally generated or added to the reactor from an external source.

2.2 FLUID BED REACTOR COMPONENTS

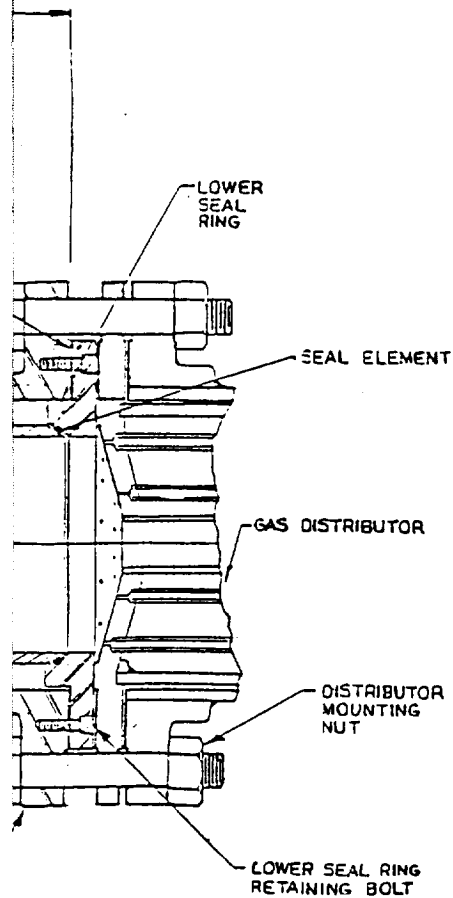
The fluid bed reactor installed and operated under the JPL contract consists of the following mechanical components:

1. Reactor shell and heaters.
2. Quartz liner with pneumatic liner sealing mechanism.
3. Feed gas plenum and distributor section.
4. Bed particle deentrainment section.
5. Product particle segregation section.
6. Product particle cooling chamber.
7. Product withdrawal valve train.
8. Downstream cooler and filters.
9. Analytical instrumentation.
10. Data acquisition equipment.

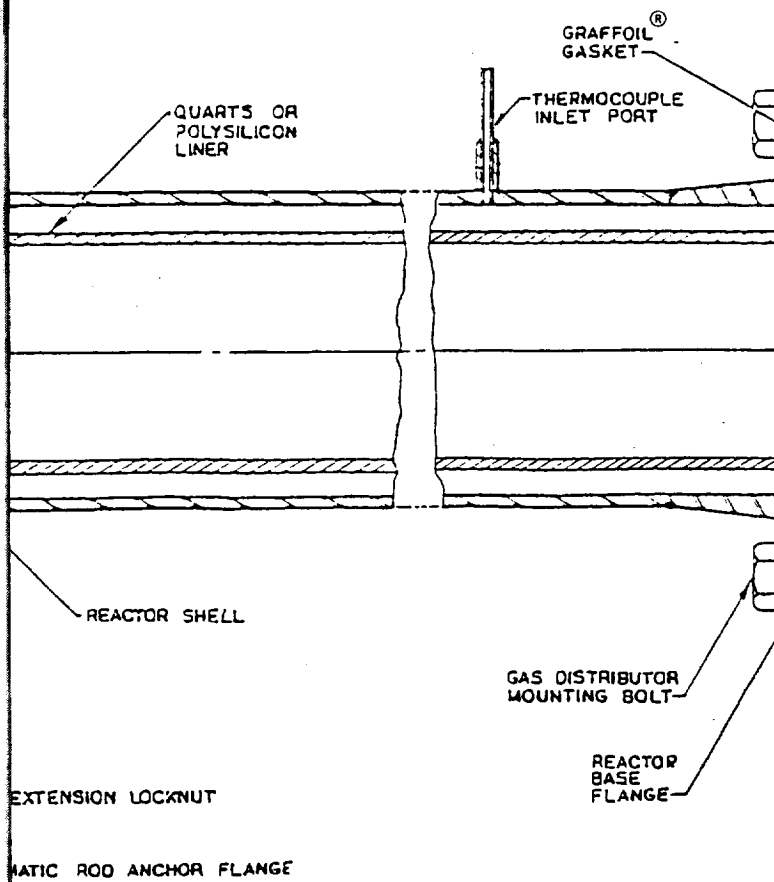
A summary description of each component follows:

2.2.1 REACTOR SHELL AND HEATERS

The reactor shell is a 6-inch, Schedule 40, 304 stainless steel pipe. The lower flange is a standard 300-lb. weld neck flange. The upper flange is modified to accommodate the pneumatic liner loading system, as well as provide the structural support point for the reactor. The shell has 1/4-inch tube fittings inserted at various heights to allow temperature and pressure measurement. Heat is provided by five independent sections of Watlow heaters. Each section is comprised of four 900-watt heaters.



FOLDOUT FRAME 2



R WITH LINER

FOLDOUT FRAME 3

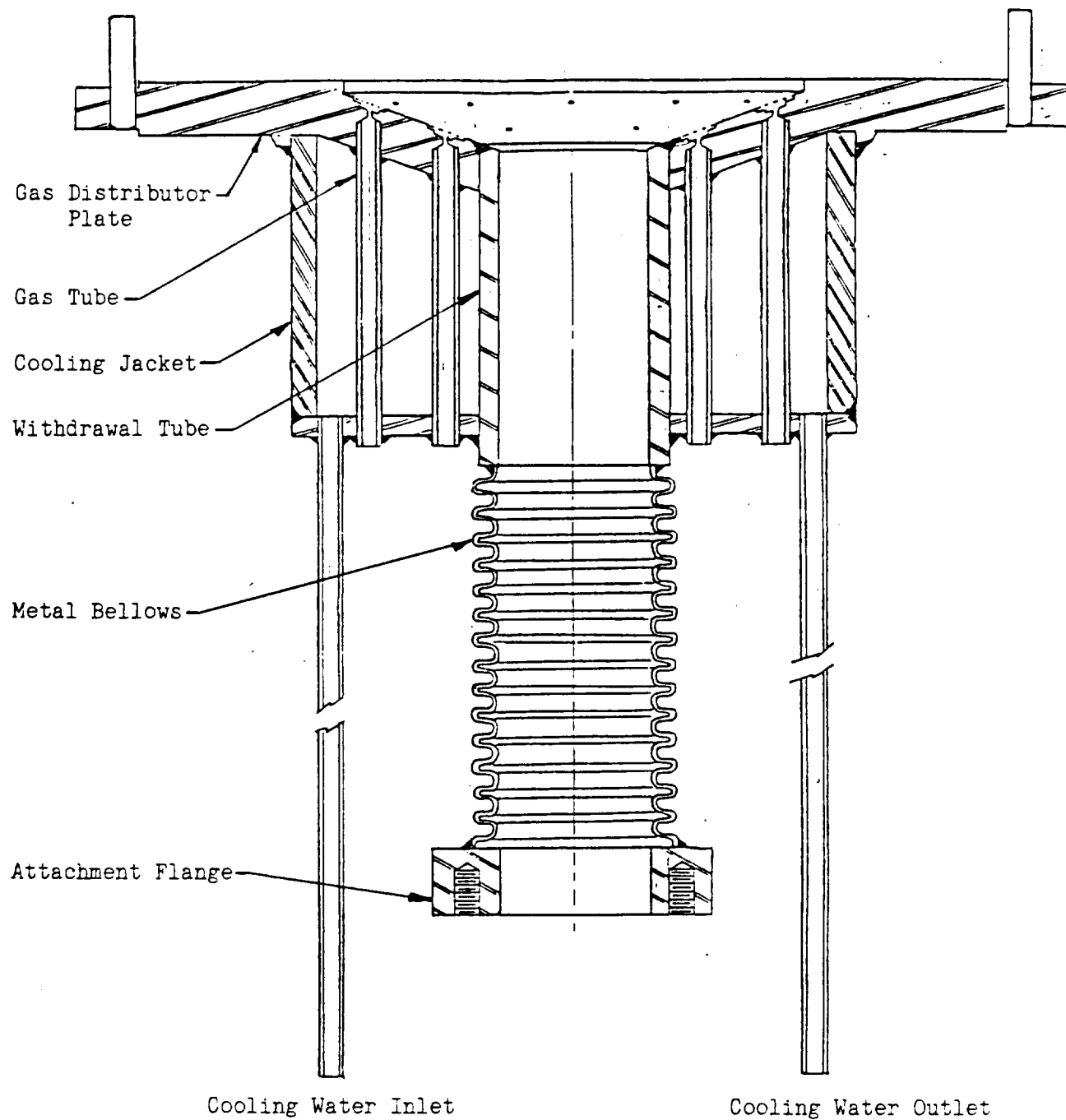


Figure 3
GAS DISTRIBUTOR

2.2.2 Liner and Seals

In order to prevent contact between the hot reactor shell and the bed material, a quartz liner is inserted in the shell. The liner is 84 inches long with polished 20° tapered ends (see Figure 2), each of which is fitted into a matching tapered steel seal piece. A gas-tight seal is accomplished by inserting a suitable copper O-ring between the two pieces. A set of 8 pneumatic cylinders provides a controlled loading of the seal to crush the copper seal ring. The bellows takes up the movement of the seal loading mechanism during heatup. Both electronic grade quartz and polysilicon have been used as liner materials.

2.2.3 Feed Gas Plenum and Distributor

The feed gas plenum consists of a short 304 stainless steel pipe section, flanged at the top and bottom. The distributor fits between the top of the plenum and the lower reactor flange. The distributor consists of a conical plate with 18 feed holes and a 1-1/2-inch opening in the center for product withdrawal (see Figure 3). A cooling chamber is attached beneath the plate. Feed gas flows from the plenum into 1/4-inch tubes and through the distributor plate. The plate feed holes consist of 0.040-inch diameter orifices covered with coarse Dynapore screen material. The orifice causes significant pressure drop to ensure good gas distribution. The screens prevent bed material from plugging the orifices when there is no flow through the distributor (e.g., during reactor evacuation before startup).

2.2.4 Deentrainment Section

The top section of the reactor consists of an 18-inch diameter expanded head. This section reduces the superficial gas velocity and prevents excessive particle carryover. However, for some experiments, this expanded head was removed and replaced by a 6-inch diameter pipe resulting in a smaller cross-sectional area increase from the lower lined region of 6.53-inch diameter.

2.2.5 Product Particle Segregation Section (Boot Section)

This section consists of a 36-inch section of 1-1/2 inch pipe, flanged at each end with a sight glass at its midpoint (see Figure 4). This section is lined with a quartz tube to prevent contact between hot particles and the metal surface.

2.2.6 Product Particle Cooling Chamber

Bolted below the segregation section is a 4-inch pipe section, tapered at the bottom to a 1-1/2-inch flange (Figure 4). This quartz lined cooling chamber is wrapped with copper cooling coils. Hot particles from the segregation section fall into the cooling chamber during product removal and are cooled for handling upon removal. Temperatures in the cooling chamber are monitored using termocouples at its inlet and outlet.

2.2.7 Product Withdrawal Valve Train

A combination of ball valves and pinch valves are utilized for product withdrawal (Figure 4). The use of ball valves for gas service and pinch valves for solids service minimizes valve abrasion by the polysilicon particles while allowing gas-tight shutoff.

The ball valves used in this section are 1-1/2-inch Whitey Series 60 stainless steel valves with teflon seats and double-acting pneumatic activators. The pinch valves are Red Valve, Series 2600, with viton sleeves. The upper two pinch valves are operated by argon to prevent air leakage into the reactor in case of sleeve failure.

2.2.8 Downstream Cooler and Filters

Effluent gas is cooled by a double pipe heat exchanger. The filters consist of 5-micron porous metal filter elements enclosed in stainless steel vessels.

2.2.9 Analytical Instrumentation

Reactor inlet and outlet gas compositions must be analyzed continually during operation. The inlet gas ranges from 0 to 60% silane in hydrogen; outlet gas ranges from 0 to 1% maximum silane.

Reactor feed gas is monitored using a Gow-Mac thermal conductivity analyzer, which provides a continuous millivolt output proportional to feed silane concentration. The output is read from a chart recorder as mole percent silane.

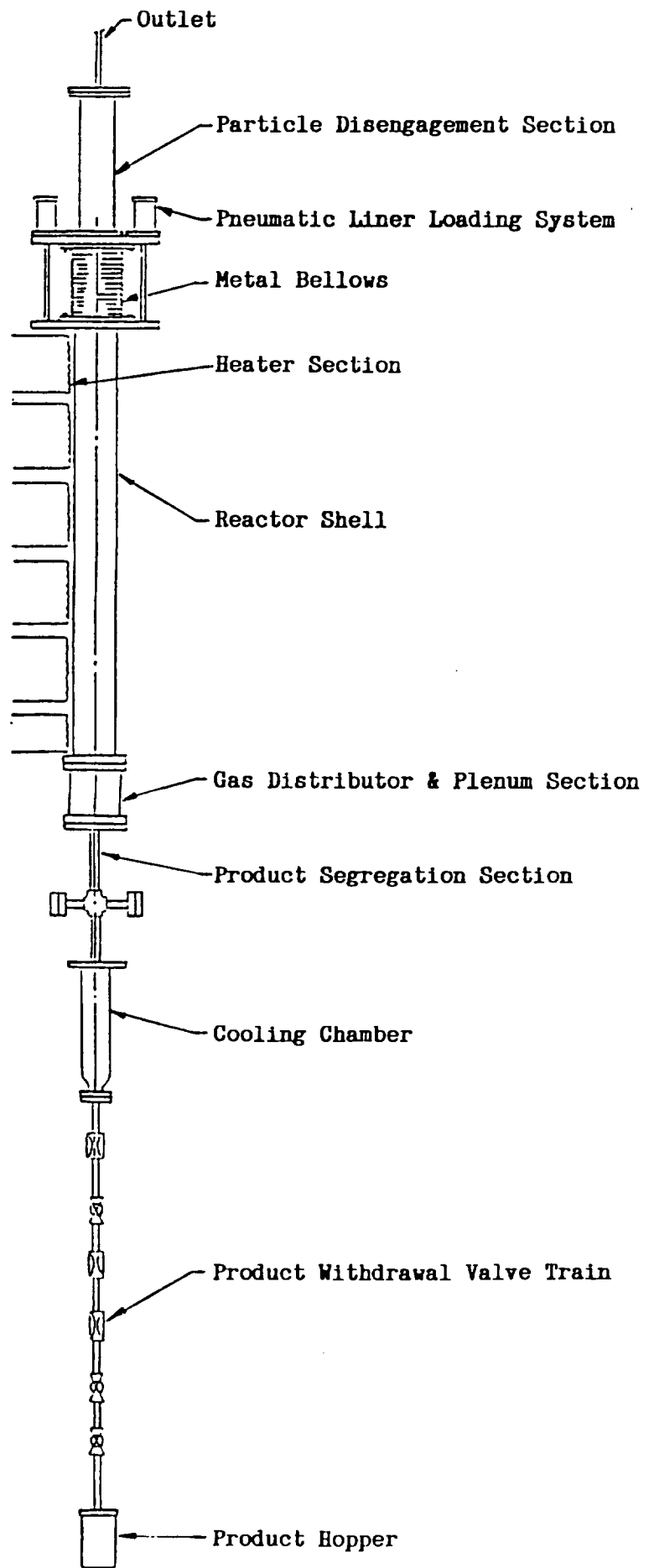


Figure 4
PRODUCT WITHDRAWAL SYSTEM

Outlet gas is monitored by a Hewlett-Packard Type 5710A gas chromatograph (GC). The GC is fitted with dual 6-foot stainless steel columns packed with Porapak Q and a thermal conductivity analyzer. A Hewlett-Packard 3380A integrator/printer translates the GC output into useable form.

2.2.10 Data Acquisition Equipment

Primary data acquisition is performed by an Analog Devices "Micro Mac". Electrical signals from the field are fed directly to this device, while pneumatic signals are fed to a Scanivalve. The Scanivalve converts pneumatic to electrical signals and feeds them to the Micro Mac. Continuous output of reactor temperatures and pressures appears on the Micro Mac display screen. Periodically, temperature and pressure data are communicated to an IBM-PC with custom software. The IBM calculates actual flow rates and fluidization velocities. This information, as well as temperature and pressure data, are sent to a printer for hardcopy.

2.3. OPERATING PARAMETERS

2.3.1 Pressure and Temperature

The reactor has been operated over a range of bed temperatures between 600° and 750°C. Specific temperatures and run results are given in Section 3.0. The reactor pressure was 10 psig at the reactor top for all runs.

2.3.2 Gas Velocities

Fluidization must be controlled for various temperatures, feed concentrations, and bed particle sizes and shapes. It is also useful to have some way of relating results of room temperature nitrogen cold model fluidization tests to reactor conditions. Throughout this program, the ratio (U/U_{mf}) between actual superficial gas velocity (U) and calculated minimum fluidization velocity (U_{mf}) has been the key parameter describing fluidization. Minimum fluidization velocity is defined as follows:

$$U_{mf} = \frac{(\phi_s \bar{d}_p)^2}{150} * \frac{\rho_s - \rho_g}{\mu} * g * \frac{\epsilon_{mf}^3}{(1 - \epsilon_{mf})}$$

- U_{mf} [=] Minimum fluidization velocity (ft/hr)
 ϕ_s [=] Shape factor
 \bar{d}_p [=] Average particle diameter (ft)
 ρ_s [=] Density of solids (lb m/ft³)
 ρ_g [=] Density of gas (lb m/ft³)
 μ [=] Viscosity (lb m/hr, ft)
 g [=] Gravitational constant (4.17x10⁸ fr/hr²)
 ϵ_{mf} [=] Void fraction at minimum fluidization

The average particle diameter is calculated by screening a bed sample into various size ranges, weighing each size range and applying the following:

$$\bar{d}_p = \frac{1}{\sum_{i=1}^n \left(\frac{x_i}{\bar{d}_{p_i}} \right)}$$

- \bar{d}_p [=] Average particle diameter (microns)
 x_i [=] Size range i weight fraction
 \bar{d}_{p_i} [=] Size range i particle size (microns)

The viscosity for a mixture of hydrogen and silane is calculated by the following equation:

$$\mu_{\text{mix}} = \frac{\sum_{i=1}^n (X_i \mu_i)}{\sum_{j=1}^n (X_j \phi_{ij})}$$

X_i = Mole fraction of species i

X_j = Mole fraction of species j

μ_i = Viscosity of species i at system temperature and pressure

$$\mu_{\text{H}_2} = \frac{(1.67493\text{E-}3) T^{1.5}}{106.087 + T}$$

$$\mu_{\text{SiH}_4} = \frac{(2.88479\text{E-}3) T^{1.5}}{227.029 + T}$$

T = Deg K

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-\frac{1}{2}} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2$$

M_i = Molecular weight of species i

M_j = Molecular weight of species j

The shape factor (ϕ_s) is a measure of the sphericity of the particle. A ϕ_s equal to one indicates a perfect sphere.

The usual procedure for determining U_{mf} is to run a cold model test using nitrogen. A 3-inch diameter clear plastic tube is charged with 2000 grams of bed material. A plot of pressure drop and bed height versus gas flow is taken. Minimum fluidization velocity is taken as the superficial gas velocity where the bed pressure drop no longer increases with gas flow. Void fraction at minimum fluidization is calculated from bed height measurements. The shape factor is then back-calculated from the minimum fluidization equation. Shape factors typically vary from 0.5 to 0.7, and the void fraction at minimum fluidization varies from 0.4 to 0.6.

Once U_{mf} , ϕ_s and E_{mf} are determined, one can relate the fluidization observed in the cold model to performance in the reactor. The velocity ratio U/U_{mf} is the primary control parameter used in determining the gas input rates. Depending on the location in the reactor, the U/U_{mf} ranges from 3 to 6.

2.3.3 Distributor Plate Temperature

In order to avoid silane decomposition in the distributor holes, the distributor plate is water cooled. This temperature is controlled below 350°C.

2.3.4 Particle Segregation Section

To maximize the segregation effects of this section, gas is fed at fairly high velocity to cause the material in the section to slug. Maintaining a U/U_{mf} of 6 to 9 results in good slugging behavior.

2.4 OUTLINE OF OPERATING PROCEDURES

2.4.1 Introduction

The following is an outline of the operating procedures for the most current fluid bed reactor pilot plant. All equipment references are found in Figure 1, Piping and Instrumentation Diagram No. 850-840-P-E021, updated 4-23-85.

Prior to startup, it is assumed that the reactor and piping have been assembled and leak tested with argon and that the bed material has been added.

2.4.2 Operation

2.4.2.1 Liner Loading

With the liner in place, loading pressure in the pneumatic cylinders is brought up to 100 psig and then backed off to 80 psig. The operator can confirm seal quality using rotometer FI-366.

2.4.2.2 Evacuation

Prior to adding any silane or hydrogen to the system, all air must be removed. It is assumed that air exists in all process and instrument lines downstream of valves 10 and 303. With the vent closed, a vacuum is pulled on the reactor, instrument and process lines, and the reactor is backfilled with argon. This cycle is repeated five times.

2.4.2.3 Purge Flows

Once the vacuum swings to reactor are complete, the following events occur:

- (a) An argon purge from CV-12 through the reactor is started. The reactor is brought up to 10 psig, and reactor pressure set on automatic control (PCV-103).
- (b) Liner shell pressure is brought up to 15 psig using FI-366. Sight glass purge (FI-451) is turned on.
- (c) Hydrogen purges through the pressure taps for differential pressure transmitters PDX-344 and PDX-348 are turned on. These purges ensure that decomposing silane does not cover and plug off the pressure taps. With no flow through the reactor (CV-12 closed, reactor at 10 psig), three rotometers (FI-443, 445, and 447) are used to balance the differential pressure transmitter outputs at zero. The net flow into the reactor from these purges, as well as any leakage through the liner seals, is then read from the downstream flowmeters (FX-108). This flow is added to reactor feed flow in the fluidization calculations.
- (d) Hydrogen purges through the Gow-Mac thermal conductivity analyzer and the GC are turned on.

2.4.2.4 Initial Heat Up

The heaters are turned on and set at 200°C for approximately eight hours.

2.4.2.5 Analytical Instrument Calibration

Both the Gow-Mac and the GC are calibrated using silane hydrogen standards. Once the calibration is complete, the standard lines are purged with nitrogen.

2.4.2.6 Final Heatup and Hydrogen Fluidization

The reactor is brought up to temperature (heater setpoint 800°C) over approximately 4 hours. During this time the argon flow is increased and the bed is fluidized. Fluidization is monitored by the two thermocouples (TE-347 and TE-522) just above the distributor. Whenever the bed settles, a noticeable temperature drop occurs here. Once the bed reaches 600°C, the argon is turned off and hydrogen is introduced through CV-312 (reactor hydrogen) and CV-320 (boot hydrogen).

2.4.2.7 Software Startup

Once under hydrogen fluidization, the IBM data acquisition program is started.

2.4.2.8 Distributor Cooling

After 30 minutes of hydrogen fluidization, the cooling water to the distributor is turned on. A distributor plate temperature set-point of 300°C is maintained.

2.4.2.9 Silane Addition

After steady distributor cooling and fluidization has been attained under hydrogen, valves 6, 10 and CV-1 are opened, PCV-15A set at 35 psi, and FCV-47 cracked open. Fluidization is monitored using calculated U/U_{mf} while the silane flow is gradually increased and hydrogen decreased. Boot segregator hydrogen is turned up to the desired U/U_{mf} . Startup is complete when silane reaches its desired level.

2.5 OPERATION

2.5.1 Maintaining Operating Parameters, Areas Requiring Frequent Checks

- (a) U/U_{mf} is maintained by changing set-points on the reactor hydrogen and silane flows (FCV-47 and FCV-313).
- (b) Bed height is monitored by a combination of bed pressure drop (PDX-344), heater section power requirements and mass balance. The frequency of product removal controls bed height.
- (c) Silane conversion is monitored by the GC, and silane in the effluent must be maintained at less than 1%. However, experience indicates that in typical operation an effluent silane concentration greater than 500 ppm is an indication of imminent difficulties. If effluent concentration reaches this level, the operator should slowly reduce silane input while maintaining silane inlet concentration (and fluidization). This reduces gas superficial velocity and increases reactant residence time. If

silane in exhaust continues increases above 1%, shutdown is necessary.

- (d) Bed temperature is monitored by thermocouples TE-347 and TE-522. These are located just above (about 0.25-inch) the distributor plate. An additional thermocouple is inserted well into the bed and away from distributor cooling effects. A drop in either of these areas indicates that the bed is underfluidized and has settled down. Flows should be increased. A continued temperature decrease indicates the formation of an agglomeration, and operation must be terminated.
- (e) Heater triac firing should be monitored. Continuous firing and lower than setpoint temperature indicate a burnt-out heater section, which should be confirmed with an ammeter. Power to the burnt-out heater should be turned off, but unless a drop in bed temperature is evident, operation can continue.
- (f) Distributor plate temperature should be maintained between 200°C and 300°C. Two control valves of different sizes are available for cooling water flow control. The water pump outlet pressure is maintained at 150 psig and should be checked periodically.
- (g) Filter pressure drop (PDX-391) must be kept below 40-inches of water. This is accomplished by periodic backblowing with hydrogen.

2.5.2 Product Withdrawal

Product is withdrawn to maintain bed height. A single product drop sequence is as follows (CV-371 and 516 are gas tight ball valves; CV-370, 372, and 373 are pinch valves all found in Figure 1):

- (a) Purge product hopper with argon.
- (b) Open manual ball valve above hopper.
- (c) Open CV-371.
- (d) Open and close CV-370 to drop bed from cooling chamber into valve train.
- (e) Open CV-372 to drop product past CV-371.
- (f) Close CV-371; open CV-516.
- (g) Open CV-373 to drop product into hopper. Open CV-372, CV-373, and CV-516.
- (h) Repeat sequence to remove desired amount of product.
- (i) Close manual ball valve. Purge hopper again and remove. Remove and seal product bag. Replace hopper with new bag in place. Purge with argon a final time.

2.5.3. Filter backblowing is done as follows:

- (a) Open CV-400 to bring filter 2 on line.
- (b) Close CV-390 to bring filter 1 off line.
- (c) Open CV-399 to vent filter plenum.
- (d) Open and close CV-394 five times to blow powder off filter.
- (e) Close CV-399; bring filter pressure up to 10 psig with CV-394.
- (f) Open CV-390; close CV-400 to bring filter 1 back into service and filter 2 off line.

2.6 CONTROLLED SHUTDOWN

Upon the completion of the run, the reactor is shut down in the following sequence:

- (a) Close valve 6; bleed silane pressure down (PI-14); close CV-1. Maintain fluidization with hydrogen.
- (b) Open CV-2 to purge silane out of lines into reactor. Purge for 5 minutes.
- (c) Open CV-12; close CV-2 and valve 10.
- (d) Turn all heater power off.
- (e) Turn off CV-303. Fluidize completely on argon.
- (f) Begin removing bed as quickly as cooling chamber temperatures permit.
- (g) With all bed material removed, reduce argon to approximately 5 SCFH. Reactor may be disassembled when cool.

3.0 EXPERIMENTAL STUDIES

3.1 SEED PREPARATION SYSTEM

The raw material for the seed consists of chunks from the breaking of electronic grade polysilicon rods grown in hot wire reactors. The broken chunks are typically 1/4- to 1/2-inch in diameter. Conversion to seed material is accomplished in two steps: grinding to size and cleaning. Grinding is done in a roll mill, and continuous screening provides the desired sizing. Cleaning and removal of metallic impurities picked up from the grinder are done using acids in an argon-agitated column.

The size reduction of the poly chunks is the most difficult step in the process. Avoiding contamination is vital, and fines production must also be minimized for economic and health reasons. Size reduction under both these constraints may be accomplished with a roll mill. Contamination is minimized by a short contact time between the rolls and the seed. Fines production in this case is also less than with other grinding devices.

The roll mill is fed manually. Material is passed through the mill three times and then transferred to the screener. This machine rejects both a coarse fraction, which is reground, and fines waste. Transfer of material to and from the mill and screener is a manual operation. Three passes through the mill are required to produce 250 micron particles from 1/4-inch feed.

The final ground and sized material is then manually transferred to the processing column, which is a clear, electronic-grade quartz tube with CPVC endpieces. The process piping is either CPVC

or PVC. Here it undergoes the following sequence of operations. First the material is washed with ultra-clean de-ionized water to remove fines and provide a wetted surface for acid addition. The seed is then cleaned for 30 minutes in a bath of concentrated HCL HNO₃ (aqua regia), which will oxidize and form soluble salts from the contaminant metals. Argon is bubbled through the column during this and the following operations to provide agitation. After 30 minutes, the seed is rinsed until a high pH is detected in the effluent. A hydrofluoric acid solution is then pumped into the column and agitated to remove silicon oxides formed through the oxidizing action of the nitric acid. Following 30 minutes of this treatment, the material is rinsed with D.I. water until the pH of the effluent reaches 5.7. The outlet stream is then routed through the resistivity meter. The rinse continues until there is no detectable increase in the resistivity of the rinse water, and the column is then drained. Interstitial water is forced out by blowing low pressure argon into the top of the column. Final drying is accomplished by applying heat and purging with argon until dry. Final seed is then dumped into poly bags and transferred to the reactor or storage.

3.2 SUMMARY OF EXPERIMENTAL RUNS

Several series of experiments were performed during this program. The experimental runs were grouped alphabetically into series. Each new series designation represented a significant change in either equipment (such as liner sealing and distributor type) or operating conditions. The table below summarizes these experimental runs.

<u>Run Series</u>	<u>Date</u>	<u>Objectives and General Description</u>
A	1st Quarter 1981	Test various heating methods, check reactor feasibility. Short runs (<15 hrs). Inlet silane <19%.
B	2nd Quarter 1982	Test of operation with seed addition. Longest run 13 hrs. Inlet silane concentration 20%. U/Umf at distributor between 7 & 8. First indication of problems with powder formation.
C	2nd Quarter 1983	Experimented with lower U/Umf ratios. Silane <22%. Longest run 11.25 hrs.
D	3rd Quarter 1983	Series of 7 experiments. Various U/Umf ratios from 2.8 to 5.5. Bed temperature 750°C. Silane concentration up to 23%. Longest run 21 hours. Produced 175micron average bed diameter from 150-micron starting material.
E	4th Quarter 1983	Silane concentration up to 25%. Longest run 25 hours. U/Umf between 3.3 to 3.8. Product size as high as 375 microns average diameter. Experimented with particle segregation in short boot segregation section. Shutdowns due to mechanical problems (e.g., heater failure, pinch valve leaks, cooling water leaks into reactor).
F	2-3rd Quarter 1984	Longest run: 24 hrs. Mechanical problems, particularly liner failure, hampered operation during this run series. Experimented with correlations estimating bed height during particle growth.

<u>Run Series</u>	<u>Date</u>	<u>Objectives and General Description</u>
G	4th Quarter 1984	Experiments using a modification of previous liner seals. Longest run: 57 hrs. Silane concentration 14%, U/Umf ~3.3. Powder formation problems.
H	1-2nd Quarter 1985	Revised liner seals, 6mm quartz liner, implemented plate type distributor during this series. First large (600+ micron) particle production with minimal powder formation.
I	3rd Quarter 1985	Tests of heat transfer through distributor plate. Attempted gas cooling of distributor.
J	4th Quarter 1985	Runs with most recent reactor design, pneumatically loaded liner with new seal design. Achieved fairly reliable operation and longest run duration to date (72 hrs). Produced 1000 ⁺ micron average diameter product.
K	1st Quarter 1986	Installed polysilicon liner with tapered seals seated in appropriate end pieces. Demonstrated ability of this liner to withstand several cycles of heatup and cooldown without cracking.

3.2.1 Experimental Run Summary H-05

This run was conducted with a quartz liner in the FBR PDU. A new perforated plate gas distributor was implemented for better gas flow distribution and more reliable temperature control. The expanded head was removed to allow for easier elutriation of fine powder from the bed.

The total run duration was 39 hours. Silane feed concentration was maintained at about 40%, although concentration levels up to 60% were tested for short durations during the run. The new distributor provided excellent temperature control and virtually eliminated the large temperature swings ($\pm 50^{\circ}\text{C}$) characteristic

of the previous Dynapore conical gas distributor. The gas distributor temperature in the present run was 300°C ($\pm 5^{\circ}\text{C}$), while the fluid bed temperature was 650°C .

At the end of 39 hours, the run was terminated due to an operator error which stopped the flow through the reactor, causing the bed to settle down. Examination of the product samples withdrawn from the bed showed the growth of large particles with virtually no fine powder. The particle size distributions in a few typical collection bags are shown in Table 1, where higher bag numbers correspond to longer residence time in the fluid bed.

It was clear that as the run progressed, the particles were growing into larger size fractions and finer fractions were being reduced. This result may be attributed to better flow distribution provided by the new distributor. Additional test runs confirmed the improved performance of the new gas distributor.

TABLE 1: PRODUCT - RUN H-05**(Particle Weight Fractions:)**

SCREEN SIZE (Microns)	BAG NUMBER (Higher number corresponds to longer residence)						
	6	8	10	12	14	16	18
840	--	--	--	--	--	--	0.01
706	0.01	--	--	0.01	0.01	0.03	0.11
600	0.01	0.02	0.03	0.05	0.05	0.09	0.15
500	0.09	0.09	0.11	0.12	0.10	0.14	0.28
419	0.15	0.14	0.15	0.15	0.15	0.24	0.29
355	0.15	0.15	0.16	0.18	0.21	0.29	0.12
300	0.14	0.15	0.16	0.19	0.24	0.17	0.03
250	0.15	0.17	0.19	0.20	0.20	0.04	0.01
212	0.13	0.16	0.13	0.09	0.04	--	--
177	0.10	0.09	0.04	0.01	--	--	--
150	0.06	0.03	--	--	--	--	--
124	0.01	--	--	--	--	--	--
Average Particle Size	294	303	331	351	361	423	510

3.2.2 Experimental Run Summary H-08

This test lasted for 39 hours and produced approximately 50 kg. of product. Feed silane concentration was maintained in the range of 10 to 20% hydrogen. The run was conducted without an expanded head on the reactor. The plate distributor used in runs H-05 through H-07 was modified for this run to avoid the earlier problem of clogged holes. The gas distributor was fitted with screen disks on countersinks above each hole which proved to be effective in eliminating clogging of holes and agglomerate formation.

The bed temperature at the bottom of the bed was in the range of 600 to 650°C. A major problem encountered during the run was some plugging of the downstream effluent line. After the bed height had increased by silane decomposition, some of the bed material was carried over due to slugging, which was responsible for the plugged effluent line. The run was continued after clearing the line. However, after 39 hours of operation, the bed was found to be settling down due to underfluidization caused by insufficient flow capacity in the feed lines. Hence, the run was terminated.

The mean bed particle size at the end of the run was determined to be 628 microns, which represents a radial growth layer thickness of 149 microns over the starting mean particle diameter of 330 microns. Table 2 presents the size distribution and the computed average particle size as a function of growth time experience by the material in the bed. The total useful product obtained from the run, excluding the starting bed material, was 50.3 kg.

The material collected in the downstream filters was analyzed for size distribution. Fine powder (< 75 microns) was 7.4% of the total silicon feed in the form of silane.

TABLE 2: PRODUCT WEIGHT FRACTIONS, RUN H-08

Duration in Bed =		12 hr	14 hr	19 hr	21 hr	25 hr	30 hr	33 hr	38 hr	40 hr
Screen	dp BAG #'s:	8	10	12	14	16	18	20	22	28
1000	1100									
841	921								0.015	0.020
707	774	0.039	0.043	0.056	0.076	0.087	0.129	0.206	0.119	0.131
600	654	0.069	0.084	0.093	0.104	0.110	0.136	0.193	0.219	0.206
500	550	0.117	0.134	0.139	0.159	0.171	0.232	0.289	0.268	0.256
420	460	0.169	0.203	0.219	0.256	0.267	0.275	0.204	0.235	0.226
355	388	0.228	0.266	0.267	0.255	0.236	0.156	0.080	0.108	0.100
300	328	0.215	0.185	0.167	0.114	0.099	0.053	0.022	0.031	0.039
250	275	0.122	0.073	0.051	0.032	0.027	0.017	0.004	0.005	0.011
212	231	0.032	0.010	0.007	0.004	0.003	0.002			0.008
150	181	.0009	0.002	0.001						0.002
75	113									
< 75	38									

average part. dia = 383 410 423 446 456 493 550 628 618

Starting bed material dp = 330 microns

Total Useful Product - Starting Bed = 50.3 kg
Total Powder = 4 kg

3.2.3 Experimental Run Summary J-02

This was the second experimental run conducted with the new PDU using a shorter, 84-inch long, quartz liner. The run lasted 58 hours and produced 102 kilograms of polysilicon product.

The quartz liner was sealed with suitable O-rings and loaded with eight pneumatic cylinders. The bellows and air cylinders were insulated and the cylinders were raised off the main loading flange to prevent thermal degradation of the cylinder packing. The expanded head was removed for this run, and a 36-inch long section of 6-inch diameter pipe was used in its place to facilitate entrainment of fine powder from the bed.

A new thermocouple was inserted through the lower liner seal flange and bent up 3 inches above the plate to provide an indication of bed temperature away from the cooling effects of the distributor plate.

The feed silane flow rate was maintained constant at approximately 55 SCFH during the course of the run. Because the total fluidization gas flow was increased with the growth of bed particle, the feed silane concentration decreased from an initial value of 20% to a final value of approximately 7%. The bed temperature at the bottom (as measured by the new thermocouple) was 650°C.

Several kilograms of product withdrawn from the bed during the run were smooth. Silane conversion was virtually 100%. After 58 hours of operation, the gas flow capacity was inadequate to maintain fluidization of the larger particles. Consequently, the

bed temperature began to drop off and the liner back-pressure dropped and could not be regained, even with large amounts of argon flow. Silane flow was then shut off, and a controlled shutdown under argon was performed.

All fines were collected in the downstream filters, with virtually no powder in the reactor product. Approximately 10% of the feed silane resulted as powder.

Mass balance for this run is shown below:

Initial Bed Weight	= 15.7 kg.
Silicon In From Silane	= <u>109.0 kg.</u>
Total	= 124.7 kg.
Product Withdrawn	= 111.2 kg.
Powder in Filters	= <u>11.3 kg.</u>
Total	= 122.5 kg.
Error in Mass Balance	= 1.8 %

Tables 3 and 4 illustrate the bed material and product sizes, respectively, for Run J-02.

TABLE 3
BED MATERIAL FOR RUN J-02

	$\bar{d}_p(\mu)$	g	wt. fr.
+ 35	548.4	18	0.0472
- 35/+40	459.8	74.3	0.1948
- 40/+45	386.1	90.5	0.2373
- 45/+50	325.2	99.9	0.2619
- 50/+60	273	71.1	0.1864
- 60/+70	229.8	11.3	0.0296
- 70/+80	194.3	4.5	0.0118
- 80/+100	163.8	3.7	0.0097
-100/+120	137.2	3.0	0.0079
-120/+140	114.3	2.9	0.0076
-140/+170	96.5	1.7	0.0045
-170/+200	81.3	.5	0.0013
-200		Trace	
		<u>381.4</u>	<u>1.000</u>

TABLE 4
RUN J-02 PRODUCT SIZES

Bag #	Hours in Reactor	Average Diameter (Microns)
Seed	0	328
13	10 1/2	348
30	26	482
38	32 1/2	562
40	33 2/3	579
52	43	729
64	54	937

3.2.4 Experimental Run Summary J-03

This was the third experimental run conducted with the new PDU using a shorter, 84-inch long quartz liner. The run was started on January 21 and fulfilled a contract objective of 72 hours of continuous operation. Total silane consumed was 93 kg., resulting in an average consumption of 1.3 kg/hr. The reactor operation was smooth, and a controlled shutdown was achieved.

Average silane feed concentration for this run was approximately 15%. The fluid bed temperature at the bottom was in the vicinity of 600°C. Fine powder collected from the filters at the end of the run was determined to be approximately 7% of the silane feed. Final bed particle diameter up to 900 microns was achieved.

Mass balance for this run is as shown below:

Initial Bed Weight	= 14.9 kg.
Silicon In From Silane	= <u>82.3 kg.</u>
Total	= 97.2 kg.
Product Withdrawn	= 86.3 kg.
Powder in Filters	= <u>5.1 kg.</u>
Total	= 91.4 kg.
Error in Mass Balance	= 6 %

3.2.5 Experimental Run Summary K-01

Run K-01 was the first run using a polysilicon liner with suitable endpieces. The primary objective of this run was to prove the ability of this liner to seal during heatup and cooldown. As a secondary test, a comparatively large amount of silane was fed to the reactor in order to check the maximum poly production that can be expected. The results of the run indicate that the poly liner can be cooled and restarted. The reactor feed concentration was run at 56% silane (123 SCFH silane) for over one hour with virtually complete conversion (<500 ppm silane in effluent). This translates to a poly production rate of 4 kg/hr usable product (after accounting for powder and wall deposition).

Equipment

A polysilicon liner with machined, tapered ends, suitable O-rings and endpieces were utilized. The coefficients of thermal expansion of the end pieces and poly were more similar. It was hoped that this would prevent the liner ends from being crushed during cool down. Because of possible difficulty drilling through the new endpieces, a bed thermocouple was not used. The liner loading mechanism, distributor and product withdrawal section were unchanged from Run J-03.

Bed Material

The bed was made up of a mixture of material from Runs J-02 and J-03. The average particle diameter was 368 microns.

The cooling chamber was filled with 11,179 grams, and the bed was filled with 16,996 grams, giving a static bed height of 58 inches above the distributor.

Operation

This run consisted of the following sequence of steps: a slow heatup; operation to determine maximum silane input; slow cool-down; reheat; return to silane; and finally, cool-down, again observing liner seal.

Heat-up was done rather slowly in order to minimize heater stress and liner thermal shock. The heaters were set at 200°C for 19 hours as a "burn-in" period. They were stepped up to operating temperature (about 800°C) over 4 hours. The reactor was allowed to heat up further for 1-1/2 hours after the heaters had attained operating temperature.

Silane was added gradually while monitoring calculated U/U_{mf} , effluent concentration and bed pressure drop. Maximum silane input (124 SCFH) was reached 21 hours into the run and maintained for just over 1 hour. Note that one of the upper heater sections had burnt out prior to this, thus reducing the maximum silane input. At 124 SCFH input, effluent silane concentration was 438 ppm. Reducing silane input to 100 SCFH lowered effluent silane below detectable limits (<1 ppm).

Once this test was completed, silane and distributor cooling water were shut off and a cool-down begun under hydrogen fluidization. Liner seal loading pressure was reduced to 20 psi. The heaters were turned down 50°C at a time. The reactor was cool enough after 8 hours to allow the burnt-out

heaters to be replaced ($\sim 50^{\circ}\text{C}$). No degradation of the liner seal was observed.

The reactor was then reheated. Operating wall temperature was reached after 7-1/2 hours. Silane was very gradually fed while closely watching the effluent concentration. Inlet silane concentration reached 23% (50 SCFH) with 100% conversion. This was maintained for 45 minutes. Final cool-down (50°C at a time) was then begun.

After the reactor reached ambient temperature, there was no evidence of seal degradation. Pressure drop and purge flow were unchanged.

Conclusion

This run indicated that the polysilicon liner with appropriate endpieces is capable of being cooled and reheated without losing its seal. This liner-seal arrangement looks very promising. The run also demonstrated the ability of the reactor to convert 56% silane feed and produce 4 kg/hr product with virtually no silane in the exhaust.

4.0 DISCUSSION OF RESULTS

4.1 PARTICLE GROWTH AND POWDER FORMATION

A primary goal of the fluid bed reactor program has been the production of a marketable sized product (1000 microns diameter) with minimal fine powder formation. The production of such a particle requires that seed particles grow at a rate sufficiently high to reach 1000 microns diameter within their residence time in the reactor. The actual radial growth rate is a function of silane feed rate, total particle surface area, and the ratio between homogeneous and heterogeneous silane decomposition. Optimum growth results from balancing all these factors. With correct conditions, growth rates as high as 24 microns per hour have been demonstrated.

4.2 POWDER FORMATION

The most persistent hindrance to good particle growth has been excessive powder formation. Silane decomposing to powder does not contribute to growth. However, powder's most detrimental effect results from its extremely large surface area per mass. Decomposition over such a large surface area can only achieve a minimal growth rate. It is vital to both minimize powder formation and remove any powder formed from the reactor.

The large amount of powder formation observed in some early experimental runs may be traced to a single primary cause: allowing any gas bubble or free space containing silane to heat above 400°C will result in powder formation. Large bubbles of feed gas

are caused by poor fluidization. Powder due to these bubbles was evident in all runs utilizing the Dynapore distributor cone. This distributor did not provide sufficient pressure drop to force good feed gas distribution. In addition, its conical shape allowed bubble coalescence even below the heated zone. Large bubbles were formed before any significant decomposition occurred. Replacing the Dynapore with a plate type distributor resulted in the first long experimental run without severe powder problems (Run H-05). Note that poor fluidization due to hole clogging in the plate distributor also causes powder problems. Installation of porous screens over the feed gas holes prevents clogging and insures good fluidization.

Allowing silane to pass through the bed into the heated free space above the bed is as detrimental as allowing poor fluidization. Silane decomposing in this area can form significant amounts of powder (e.g. Run J-01). Due to the slugging action of the bed, it is difficult to eliminate the heated walls above the bed. Therefore, all silane must be converted in the bed to minimize the powder.

In addition to minimizing powder formation, it is important to remove what powder is formed from the bed. The powder is detrimental due to the surface area effect noted earlier. Any significant fraction of powder in the bed can also severely deteriorate fluidization. This causes additional powder formation and eventually will force a shutdown. The reactor must be designed to entrain the fine material while retaining the desired bed particles. Experiments with the PDU indicate that the 18-inch diameter expanded head retains excessive amounts of fines. The ratio of areas between

this head and the reactor is 15.8:1. Use of a 6-inch pipe section (area ratio 1.75:1) proved more acceptable. Cold model tests indicated that an area ratio of 4:1 would be ideal.

Once all the above conditions were fulfilled (Runs H-05, H-08, J-02, J-03, K-01), powder was acceptably low (7-10% of silicon feed as collected in the filters). Powder observed in the product was negligible.

4.3 SILANE FEED CONCENTRATION

Although it is desirable to feed as high a concentration of silane as possible, a number of factors limit the actual feed concentration. A silane feed concentration of 57% was fed to the reactor during Run K-01 without difficulty. However, typical feed concentrations were limited to below 30%. Higher feed silane concentration can result in powder formation purely due to mass transfer effects. Silane in the gas can reach decomposition temperature before reaching a bed particle surface, resulting in homogenous decomposition. The concentration at which this becomes significant is not yet clear.

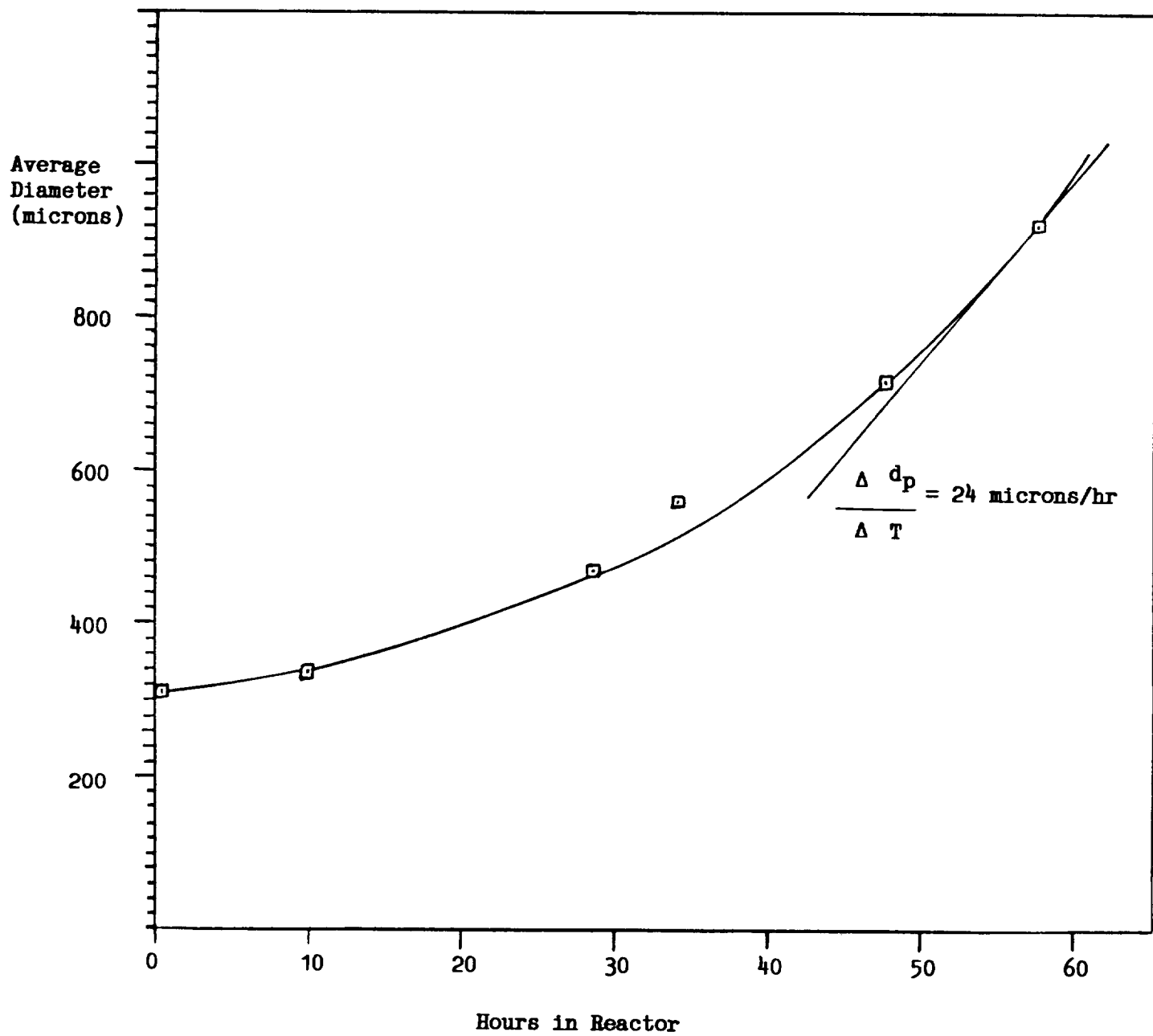
Experimental feed concentration was limited by more practical concerns as well. It was observed that adding silane to a bed fluidized on hydrogen causes a cooling effect just above the distributor. With too much silane, this can become severe and cause the bed to settle down. Reactor capacity was limited by the reactor's heated area. Complete conversion of higher feed concentrations requires longer residence time.

Table 5 shows a summary of recent experimental runs and average silane feed concentrations for these runs. The particle growth as a function of time is illustrated in Figure 5 for Run J-02. Toward the end of this run, growth rates up to 24-microns/hr. were achieved.

TABLE 5
SUMMARY OF RECENT RUNS WITH AVERAGE SILANE
FEED CONCENTRATIONS

<u>RUN</u>	<u>DATE</u>	<u>DURATION (HRS)</u>	<u>AVG. SILANE CONCENTRATION</u>	<u>COMMENTS</u>
H-01	2/ 5/85	7	28%	Quartz Liner
H-02	2/19/85	21.5	28%	Powder Problems
H-03	3/18/85	8	33%	
H-04	4/ 1/85	34	25%	
H-05	5/ 6/85	39	40% Max. 60%	New Distributor, Minimal Powder
H-06	5/29/85	2	10%	Distributor Clogging
H-07	6/18/85	6	10%	
H-08	7/24/85	39	15%	Added Screens to Distributor Holes
J-01	11/21/85	54	23%	First Run with Shorter Reactor & New Liner-Seal
J-02	12/17/85	58	18%	High Growth Rates (24 microns/hr)
J-03	1/21/86	72	15%	Longest Run, 1mm Product
K-01	2/11/86	22	7-57%	Poly Liner

FIGURE 5. PRODUCT MATERIAL RUN J-02



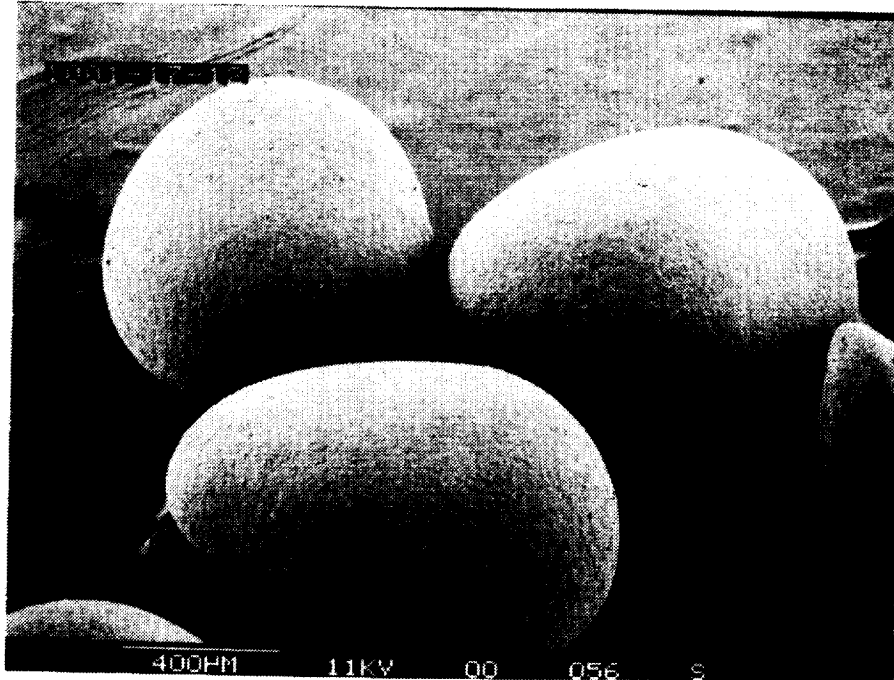
4.4 PRODUCT MORPHOLOGY

Numerous scanning electron micrographs (SEM's) were taken of the fluid bed product in various forms. Included here are: 1) whole product particle; 2) high magnification of product surface; 3) a shattered particle; and 4) a mounted and polished particle cross-section.

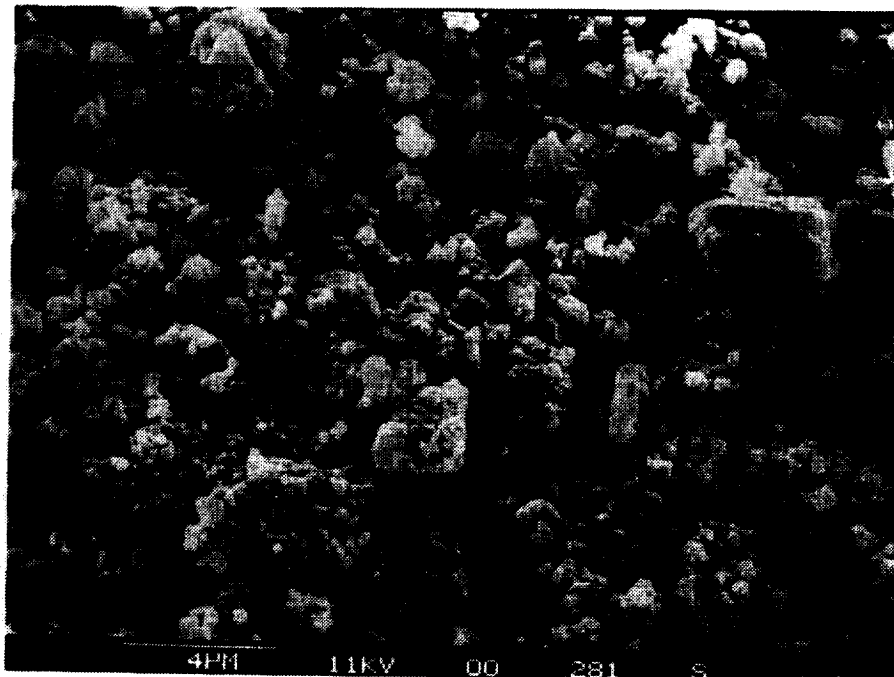
The most striking observation of fluid bed product (in contrast to rod poly) is its dusty, grey surface. This is quite evident when one handles product material. Small amounts of fine powder can be abraded off the particle surface. Chemical etching of the product surface has no visible effect on surface gloss. It has been noted that an ultrasonic wash using a detergent mix will give the product a smoother surface. The SEM picture of the product shows a rounded, porous surface (Photo 1). Close up of this surface (Photo 2) shows a porous agglomeration of submicron powder. This could explain why etchant had little effect, whereas the detergent surfactant resulted in a slightly cleaner surface (by lifting off the powder). Photo 3 indicates that the growth layer may not be as hard as the seed. It appears that the growth layer has merely chipped off of the seed core. The particle cross-section (Photo 4) shows porous growth rings. These all suggest that the particle growth may be a combination of silane decomposition on the particle surface and scavenging of residual fines. The growth rings seen in the particle cross-section indicate that the scavenging may be periodic. As the particle

migrates into the high silane concentration area near the distributor, heterogeneous decomposition may occur. The particle eventually is forced up through the bed where the silane concentration is lower. With the depletion of the silane in the boundary layer surrounding the particle, homogeneous decomposition with powder scavenging may become predominant. In any case, the product morphology indicates that the actual mechanism of particle growth is much more complex than pure heterogeneous decomposition growth.

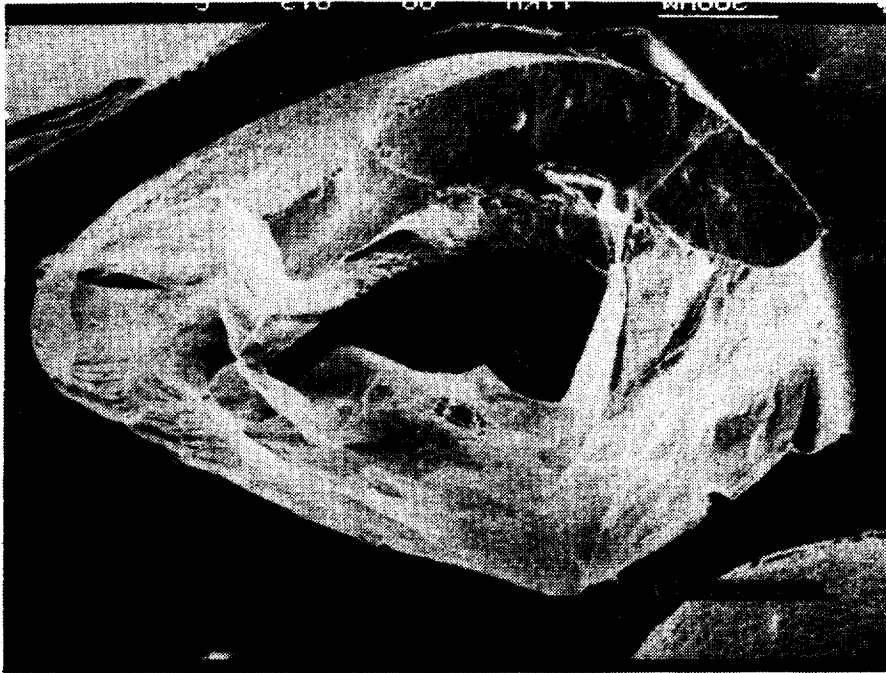
SEM pictures of product samples from Run J-02 are shown in Photos 5 and 6. These pictures illustrate the growth of approximately 1 mm diameter particles, with a smooth exterior surface.



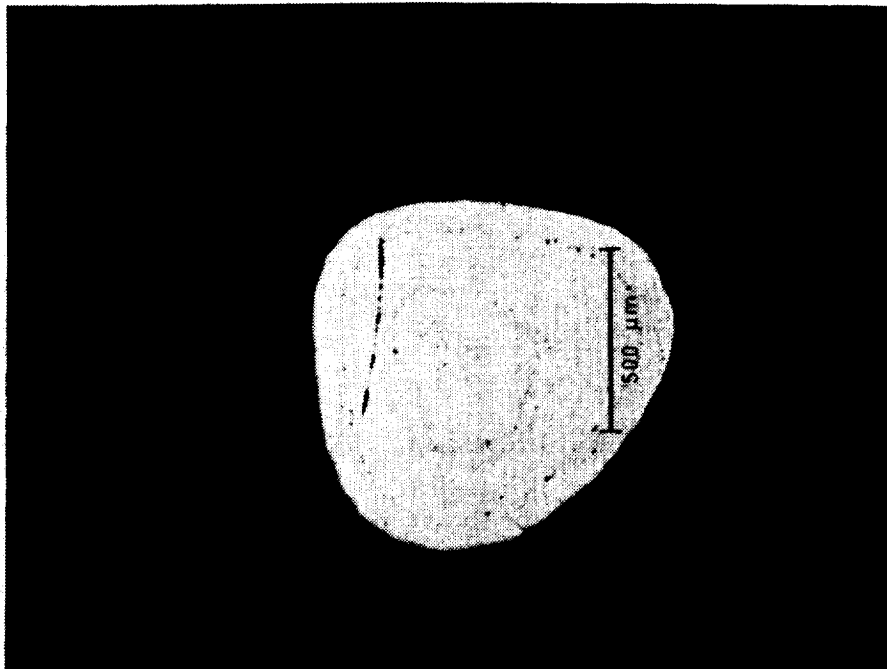
1. Product



2. Product Surface

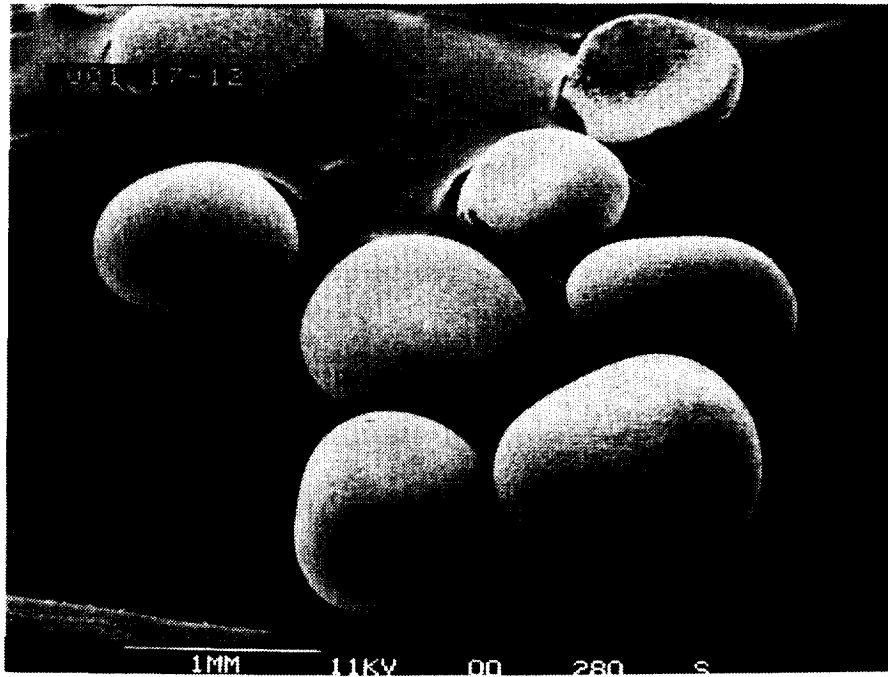


3. Shattered Product Particle

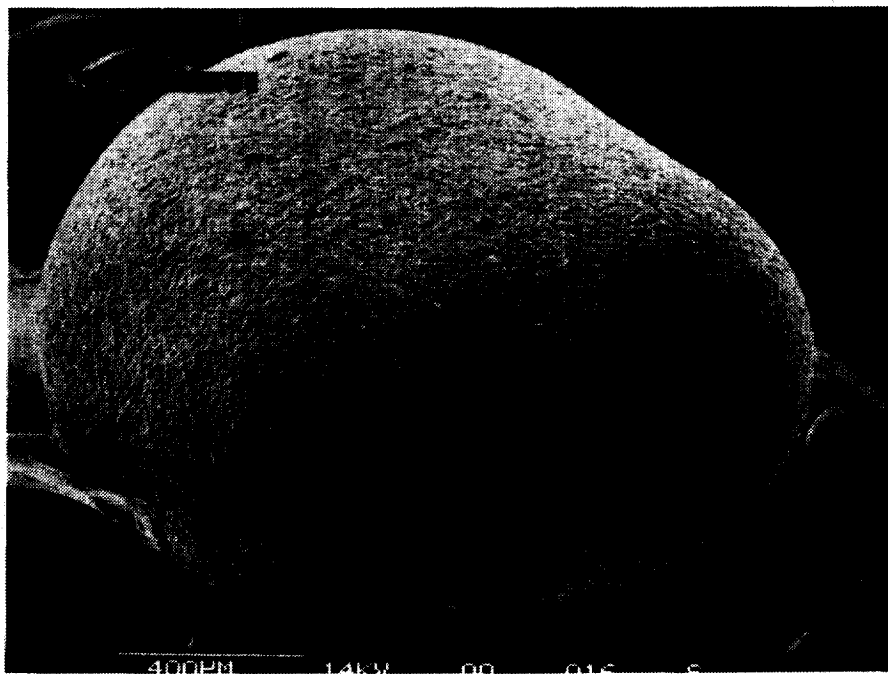


4. Particle Cross Section

SEM PICTURES OF PRODUCT FROM RUN J-02



5.



6.

4.5 CHEMICAL ANALYSIS OF SAMPLES

4.5.1. Seed Purity Results

A number of seed samples were sent out for analysis. Analysis of seed material prepared prior to construction of the present seed cleaning system is included for reference. The Table 7 below gives sample descriptions and analysis results. The analyses used were emission spectroscopy (ES) and neutron activation analysis (NAA).

4.5.2. Analysis of Early Seed Material

The following tests were performed on material crushed using the shatterbox (roll mill predecessor). The samples and treatments were as follows:

<u>SAMPLE NO.</u>	<u>DESCRIPTION</u>	<u>ANALYSES</u>
001-13-1:	Raw seed-crushed and screened but not cleaned.	ES
001-13-2:	Cleaned in a sulfuric acid-hydrogen peroxide mixture for 30 min. followed by treatment with dilute HF for 30 min.	ES
001-13-3	Cleaned in a dilute HCl-HNO ₃ mixture for 5 min. followed by dilute HF treatment for 5 min. This duplicated cleaning steps previously used to prepare fluid bed seed.	ES
001-13-4:	Cleaned in concentrated HCl-HNO ₃ for 30 min. Treated with dilute HF for 30 min.	ES

4.5.3. Analyses of Recent Seed Material and Product

The following analyses were performed on material crushed in the roll crusher, screened and treated with the seed preparation system:

<u>SAMPLE NO.</u>	<u>DESCRIPTION</u>	<u>ANALYSES</u>
001-15-1:	Material cleaned for Run J-01, bag #2-5.	ES
001-15-2:	Material cleaned for Run J-01, bag #2-3.	ES
001-15-3:	Material cleaned for Run J-01, bag #1-5.	ES
001-15-4:	Seed for J-01, crushed and screened but not cleaned.	ES
001-15-6:	Material cleaned for Run J-01, bag #1-5.	NAA
001-15-7:	Material cleaned for Run J-01, bag #1-5.	NAA
001-17-1,2,9,10:	Cleaned seed for J-02.	NAA, ES
001-18-1:	Cleaned seed for J-03	NAA
001-18-2:	Product from run J-03	NAA
001-18-3:	Product from run K-01	NAA

TABLE 6

SEED MATERIAL ANALYTICAL RESULTS

PPM Impurities - Emission Spectroscopy

<u>SAMPLE #</u>	<u>Cr</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Mo</u>	<u>W</u>	<u>Al</u>
001-13-1	140	380	-	45	2.5	-	-	<20
001-13-2	<10	<40	-	<10	<1	-	-	110
001-13-3	120	260	-	34	1.2	-	-	<20
001-13-4	<10	<40	-	<10	<1	-	-	<20
001-15-1	< 8	-	-	-	1.8	-	-	-
001-15-2	< 8	-	-	-	1.3	-	-	-
001-15-3	< 8	-	-	-	0.52	-	-	-
001-15-4	< 8	-	-	-	0.99	-	-	-

PPM Impurities - Neutron Activation Analysis

<u>SAMPLE #</u>	<u>Cr</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Mo</u>	<u>W</u>	<u>Al</u>
001-15-6	9.7	42	0.18	3.2	-	0.096	1.4	-
001-15-7	7.0	25	0.22	1.6	-	0.073	1.3	-
001-17-1	0.35	1.6	0.0063	0.11	0.0092	0.0057	0.0021	-
001-17-2	0.89	3.5	0.009	0.39	0.015	0.086	0.0085	-
001-18-1	3.3	15	0.043	1.0	0.027	0.030	.071	-
001-18-2	0.046	0.23	0.0006	0.018	0.0081	0.00085	0.00015	-
001-18-3	0.066	3.1	0.011	0.26	0.043	0.010	0.001	-

Typical purity analyses for seed and product are compared in Tables 8, 9 and 10. In general, the product growth layer has less contamination than the starting seed material.

TABLE 7

PURITY ANALYSIS FOR SEED AND PRODUCT SAMPLES
FOR RUN H-04 BY SSMS

	<u>Seed, ppma</u>	<u>Product, ppma</u>
Fe	≤ 0.5	< 0.5
Al	1	0.5
Cr	0.03	0.03
Mn	0.03	≤ 0.02
Ni	< 0.5	< 0.5
Cu	≤ 0.02	≤ 0.02

TABLE 8

PURITY ANALYSES FOR SEED AND PRODUCT SAMPLES
FOR RUNS J-02, J-03, K-01 BY SSMS

	PPMA					
	J-02		J-03		K-01	
	Seed (NAA)	Product	Seed	Product	Product	
Fe	1.6	1.0	3.0	1.0	1.0	
Cr	0.35	0.05	0.1	0.05	0.05	
Al	N.A.	0.05	1.0	0.5	0.5	
Ni	0.11	< 0.05	≤ 0.1	< 0.1	≤ 0.1	
Cu	N.A.	0.05	0.05	0.05	0.03	

TABLE 9

PURITY ANALYSIS FOR PRODUCT SAMPLES
FROM RUNS J-03 AND K-01 BY NAA

	<u>J-03, ppm</u>	<u>K-01, ppm</u>
Fe	0.23	3.1
Cr	0.046	0.066
Ni	0.018	0.26
Cu	0.0081	0.043
Mo	0.00085	0.01
W	0.00015	0.001

4.6 SINGLE CRYSTAL GROWTH

Product from run H-02 was crystallized by Hamco. A 3-inch diameter by 21-inch long dislocation-free crystal was obtained, followed by 7-inches of dislocated single crystal and 4-inches of polycrystalline material. Wafers sliced from the top and bottom ends (excluding the poly region) were analyzed by FTIR for donor, acceptors, carbon, and oxygen. Resistivity measurements were made on the wafers using a four-point probe. The results are shown below:

	<u>TOP END</u>	<u>BOTTOM END</u>
Phosphorus, ppba	4.2	8.5
Boron, ppba	8.5	10.0
Arsenic, ppba	0.1	0.28
Aluminium, ppba	1.2	4.6
Antimony, ppba	< 0.02	0.7
Carbon, ppma	4.99	22.0
Oxygen, ppma	14.0	18.0
Calculated Resistivity, ohm-cm	50 p-type	40 p-type
Measured Resisitivity, ohm-cm	87 p-type	87.6 p-type
(Average of 10 points)		

The above data indicate significant improvements to the product purity, compared to earlier samples. A significant portion of contamination in the above product is believed to originate from the starting seed material. With the use of an improved system for seed preparation and with the growth of larger diameter product particles, the fluid bed process can effectively produce semiconductor-grade silicon.

5.0 TECHNICAL ASSESSMENT

5.1 PROCESS

The present work with a 6-inch diameter process development unit has demonstrated that silane decomposition can be efficiently accomplished in a fluidized bed reactor to produce high purity silicon particles. Several long-duration test runs were conducted, the longest single continuous run being of 72 hours duration. In these runs, the feed silane concentration was typically in the range of 25 to 30% in hydrogen, although concentrations up to 50% were tested for short intervals. Virtually complete silane conversion was achieved in the reactor, with over 90% of the feed silane contributing to particle growth. Fine powder was usually in the range of 5 to 10% of the silane feed. Seed particles of an initial mean size of 300 microns were grown to approximately 1000 microns.

The fluid bed product particles from the above tests displayed a smooth, rounded exterior surface with a ring-like, layered structure. The particles have a uniform deposition morphology with a bulk density of approximately 1.6 gm/cc. The particles are free-flowing and can be transferred from one vessel to another either pneumatically or by gravity.

Analysis of seed and product samples for heavy metals showed that the deposited growth layer is of higher purity compared to the seed material. Comparison of product purity from samples generated in unlined and lined reactors clearly demonstrated that the liner is an effective impurity barrier from the reactor walls.

The fluid bed product can be melted in a Czochralski furnace. The present work demonstrated the feasibility of growing a dislocation-free single crystal of high intrinsic resistivity. This process is thus well suited for the production of high purity polycrystalline silicon.

5.2 ECONOMICS

An order-of-magnitude cost estimate for a commercial scale polysilicon facility based on fluid bed technology was prepared. This estimate was done on the basis of using four quartz-lined fluid bed reactors of 12-inch internal diameter and 5-inch bed height to generate 1000 MT/year of product. Silane production facility cost was not part of this estimate. Total capital investment for the fluid bed system was estimated at \$7.2 MM in constant 1985 dollars, and the associated annual operating cost was estimated at \$5.53 MM.

Based on the above order-of-magnitude estimates, the incremental product cost, excluding the cost of silane, was calculated to be \$6.1/kg. silicon at 0% DCF rate of return and \$10.26/kg. of silicon at 30% DCF rate of return.

Several other economic analyses tend to support the contention that the fluid bed process has the lowest product cost compared to other hot-wire type deposition techniques. Shimizu⁽⁴⁾ of Osaka Titanium Co, Japan, conducted such a comparative economic study and concluded that the NEDO and the Union Carbide Corporation-JPL fluid bed processes have the greatest probability for producing low-cost silicon. The silicon cost in this study was estimated to be ¥ 5400/kg., approximately 50% of that from the conventional Siemens

Process. Reiter⁽⁵⁾ of JPL conducted a probabilistic analysis of silicon cost for three different processes. He concluded that the prospects for reaching the DOE cost goal is most promising for the Union Carbide fluid bed process, with greater than a 90% chance that the fluid bed product will cost less than \$20/kg. (1982 dollars).

It is thus believed that the fluid bed process offers the best chance of producing high purity polycrystalline silicon at a cost which is consistent with DOE/JPL FSA cost goals.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions may be drawn from the recent fluid bed experimental work:

1. Complete silane decomposition can be achieved in a compact fluid bed reactor, and over 90% of the silane fed to the reactor can be deposited on silicon seed particles.
2. Seed particles of average diameter of 300 microns can be grown into a product of over 1000 microns in diameter.
3. A 6-inch diameter fluid bed reactor can be operated efficiently with silane feed concentrations in the range 25 to 30% in hydrogen. Operation with higher silane feed concentrations up to 50% is feasible.
4. The fluid bed product consists of smooth, round, free-flowing particles which have a good deposition morphology.
5. Quartz and polysilicon liners are both suitable for serving as good impurity barriers from the reactor wall. The liner can be effectively sealed from the outer shell. Quartz liner tends to break during the final cool-down cycle due to thermal stresses, whereas a polysilicon liner can be reused.
6. With suitable procedures for preparing high-purity seed particles and for handling the product particles, the fluid bed process can produce semiconductor-grade product for photovoltaic and other applications.
7. The fluid bed product can be melted in a Czochralski furnace. The growth of high-resistivity, dislocation-free, single crystals is feasible.
8. The fluid bed process offers the most attractive route for producing low-cost silicon, consistent with DOE/FSA cost goals.

Future development should be directed in the following areas to commercialize this technology:

1. A method for generating semiconductor quality seed particles, either internal to the reactor or externally, should be developed.
2. The reactor should be operated for long durations in steady state with respect to the particle size. In this mode, the mean particle size in the reactor would remain constant with respect to time. Coarse particles would be preferentially withdrawn as product, while seed particles would be introduced into the bed.
3. Suitable procedures should be developed for handling the fluid bed product without introducing contaminants. The product should be withdrawn from the reactor, packaged, and introduced into the crystal growth chamber without exposure to the atmosphere.

7.0 REFERENCES

1. Low Cost Solar Array Project, "Feasibility of the Silane Process for Producing Semiconductor Grade Silicon", Final Report for the period Oct 1975 - Mar 1979 by Union Carbide Corporation, June 1979.
2. Flat Plate Solar Array Project, "Experimental Process System Development Unit for Producing Semiconductor Grade Silicon Using the Silane to Silicon Process", Final Report Phase III for the period Apr 1979 - Dec 1981 by Union Carbide Corporation.
3. Iya S.K., Flagella R.N., DiPaolo F.S. Heterogeneous decomposition of silane in a fixed bed reactor. J. Elec. Chem. Soc., Vol. 129, No. 7, July 1982.
4. Proceedings of the Flat Plate Solar Array Project Workshop on Low-Cost Polysilicon for Terrestrial Photovoltaic Solar Cell Applications, JPL Publication 86-11, Feb 1986.
5. Reiter L.J. A probabilistic analysis of silicon cost. JPL Publication 83-94, Nov 1983.